Recommendations

for a

STATE OF CALIFORNIA CERTIFICATION PROTOCOL FOR ALTERNATIVE CLEANING CHEMISTRIES

Prepared by
Lawrence Livermore National Laboratory
and the Alternative Cleaning Chemistries Stakeholder Panel

for

California Environmental Protection Agency
Department of Toxic Substances Control
Office of Pollution Prevention and Technology Development

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

Page 2 Rev 24 2/9/98

Acknowledgments

These recommendations were prepared by Lawrence Livermore National Laboratory (LLNL), Livermore, California, under Agreement Number 95-T0983 (Task 3) between the U.S. Department of Energy and the California Department of Toxic Substances Control. The LLNL Principal Investigator and lead author for this project was Dr. Michael Meltzer, and Katharine Gabor was a contributing author. Both authors are members of LLNL's Pollution Prevention Group, which operates within the Operations and Regulatory Affairs Division of the Laboratory's Environmental Protection Department.

This document was prepared with guidance from the Alternative Cleaning System Stakeholder Panel, whose members are listed below. The panel was assembled expressly for this project, and their many suggestions were received with appreciation by the authors.

Alternative Cleaning Chemistries Stakeholder Panel

Panel Member	Credentials	Organization
Mike Beeks	Chemist and Cleaner	Brulin Corporation
	Manufacturing	
Tom Barron	Engineer/P2 consultant	Thomas S. Barron, PE
Mike Callahan	Chemical Engineer	Jacobs Engineering Group -
		Environmental Services
Dr. Anupom Ganguli	Senior Manager, Stationary	South Coast Air Quality Management
	Source Compliance	District
Louie Yuhas	Supervisor, Air Quality	South Coast Air Quality Management
	Analysis and Compliance	District (alternate representative)
Dr. Cal Kodres	Mechanical/Environmental	Port Hueneme Naval Facilities
	Engineer	Engineering Service Center
Kraig Kurucz	Chemical/Environmental	Lockheed/Martin Missiles & Space
	Engineer	
Joe Lukas	Chemist and Cleaner	Inland Technology Incorporated
	Manufacturing	
Zelco "Z" Halar	R&D Director	Inland Technology Incorporated
		(alternate representative)
Jim Miille	Chemist/P2 Consultant	Chemical Solutions Inc.
Dr. Jim Seward	Occupational Physician	LLNL Health Services
John Mukhar	Civil/Environmental	City of San Jose Environmental Services
	Engineer	Department/San Jose-Santa Clara Water
		Pollution Control Plant
Ted Smith	Attorney	Silicon Valley Toxics Coalition
Dennis Zupan	Senior Chemist	Brulin Corporation

In addition to the panel members noted above, the following individuals contributed helpful comments, data, or other assistance to the authors. Their support is gratefully acknowledged.

Panel Guests	Credentials	Organization
Ron Block	President	Block Environmental Services
John Butenhoff	Manager, Toxicology Services	3M Specialty Chemicals
Corazon Choa	Principal Air Quality Chemist	South Coast Air Quality Management
		District
Victor Douglas	Air Resources Engineer	Air Resources Board
Rudy Eden	Laboratory Services Manager	South Coast Air Quality Management
		District
Alex Ekster	Associate Sanitation Engineer	City of San Jose Environmental Services
		Department/San Jose-Santa Clara Water
		Pollution Control Plant
Virginia Lew	Industrial Hygienist	LLNL
Mike Morris	Program Manager	Institute for Research & Technical
		Assistance
Karna Peters	Attorney, attending for 3M	Peters & Peters
Lael Pickett	Chemist	3M Specialty Chemicals
Kathleen Wolf	Executive Director	Institute for Research & Technical
		Assistance
Kurt Werner	Toxicology Specialist	3M Specialty Chemicals

Finally, the authors wish to express their gratitude for the guidance provided by Kim Wilhelm and Phil Loder of the California Department of Toxic Substances Control.

Table of Contents

INTRODUCTION	7
STAGE A: SCREENING CRITERIA	9
A. 1.0 Make-or-Break Criteria	9
A. 1.1 Global Environmental Impacts	9
A. 1.2 REGIONAL ENVIRONMENTAL IMPACTS	10
A. 1.3 Human Health Impacts	11
A. 1.4 CAUTIONARY SUBSTANCES	13
A. 2.0 Performance Verification	13
A. 3.0 Vendor Responsibility	14
A. 4.0 SITE INSPECTION	16
STAGE B: ASSAYS, DATA-BASE SEARCHES AND MODELING	17
B. 1.0 Acute Toxicity	17
B. 2.0 Chronic Toxicity	
B. 3.0 Environmental Impact	19
APPEALS PROCEDURE	20
PERIODIC REVIEW REQUIREMENTS	21
TABLES	

Introduction

This protocol contains recommendations for Applicants seeking a California-EPA Alternative Cleaning Chemistry Certification. The purpose of the certification is to identify cleaning chemistries whose use will help reduce health and environmental risks associated with industrial cleaning operations, without sacrificing cleaning performance.

Candidate chemistries will be evaluated to determine whether they qualify for an Alternative Cleaning Chemistry Certification, as well as to identify the class of certification that is appropriate for qualified chemistries. A cleaning chemistry is eligible for approval in one or more of the following classes of certification:

- **Precision metals cleaning:** for parts produced in close tolerance electroplating, machining, casting, and other types of metal fabrication operations.
- **Precision electronics cleaning:** for printed circuit board, semiconductor, and electronic component cleaning operations.
- **General purpose cleaning:** for less demanding applications such as automobile repair shop cleaning.

Regulatory Basis and Intent of Certification Program

Effective January 1, 1994, Chapter 412, Statutes of 1993, Section 25200.1.5, *Health and Safety Code* (enacted by California State Assembly Bill 2060, Weggeland) authorized the California-EPA's Department of Toxic Substances Control (DTSC) to certify the performances of hazardous waste environmental technologies. Such environmental technologies must meet both specific criteria noted below before being certified.

- They must be determined not to pose a significant potential hazard to the public health and safety or to the environment, when used under specified operating conditions.
- They can be operated without specialized training, and with minimal maintenance.

The purpose of the certification program is to provide a comprehensive, independent review of technologies to facilitate regulatory and end-user acceptance, and to promote and foster the growth of California's environmental technology industry.

Manufacturer's responsibilities

By accepting certification, the manufacturer will assume, for the duration of the certification, responsibility for maintaining the quality of the manufactured equipment and materials at a level equal to or better than was provided to obtain certification. Furthermore, the manufacturer will agree to quality monitoring by DTSC, as required by the statute under which a certification is granted.

Collaboration with South Coast Air Quality Management District (SCAQMD)

The criteria described below include the requirements of SCAQMD's Clean Air Solvent (CAS) Certification Protocol. The laboratory analyses necessary to verify compliance will be performed by SCAQMD, or, if a reciprocal laboratory agreement is formed, at a DTSC laboratory. The analyses can also be performed at SCAQMD-approved private laboratories. The test protocol will be uniform at all laboratories verifying compliance.

DTSC will forward a sample of the candidate cleaning chemistry, in its concentrated form, to the analysis laboratory. The analysis laboratory will evaluate the sample for Volatile Organic Hazardous Air Pollutants (VOHAPs), Ozone Depleting Compounds (ODCs), Global Warming Potential compounds (GWPs), reactive components, and total Volatile Organic Compound (VOC) concentration. The SCAQMD laboratory's detection limit for compounds fitting the above categories is **0.01**% of the concentrated form of the cleaning chemistry. Alternatively, if the candidate cleaning chemistry already holds an SCAQMD CAS certification, the Applicant will submit a copy of that certification, along with a copy of the test results from the SCAQMD laboratory.

If a CAS certificate issued by SCAQMD is later revoked by that agency, any alternative solvent certification issued by DTSC would also be revoked.

Format of Criteria Recommendations

Two stages of criteria are suggested. Stage A includes **Make-or-Break** criteria, an initial screen for candidate cleaning chemistries. (See **Section A. 1.0** for an explanation of Stage A discriminators.) Also included in Stage A are criteria that use anecdotal evidence to verify that the cleaning chemistry is able to achieve a high level of performance, and vendor literature to verify that the vendor has met its responsibilities for clear operating instructions and accurate information on hazards associated with the chemistry.

Stage B criteria involve more in-depth analyses of the candidate cleaning chemistry, employing biological and environmental assays, database research, and toxicological modeling approaches.

Page 8 Rev 24 2/9/98

STAGE A: SCREENING CRITERIA

Stage A. 1.0 Make-or-Break Criteria

The make-or-break criteria provide an initial screening to eliminate cleaning chemistries that are perceived to pose an unacceptable risk to human health or the environment. The make-or-break criteria are simple, easily applied discriminators. They employ readily available information, in contrast with the other criteria that involve comprehensive analysis of the candidate cleaning chemistry. The make-or-break criteria include all SCAQMD CAS requirements, which focus on air quality, as well as other requirements covering releases to other media. Make-or-break criteria are grouped into the following areas of concern:

- Global environmental impacts.
- Regional environmental impacts.
- Human health impacts.
- Cautionary substances.

A. 1.1 Global Environmental Impacts

A. 1.1.1 Ozone Depletion Potential (SCAQMD Clean Air Solvent requirement)

No cleaning chemistry shall be certified when it contains more than 0.01% of chemicals defined as stratospheric ozone depleting compounds (ODCs). **Table 1**, developed by SCAQMD, lists known ODC's.

A. 1.1.2 Global Warming Potential (SCAQMD Clean Air Solvent requirement)

No cleaning chemistry shall be certified when it contains more than 0.01% of chemicals on the SCAQMD "Compounds with Global Warming Potential" list,¹ with the exception of CO₂ that is used in such a way as to not increase the net CO₂ inventory of the atmosphere.² The SCAQMD list is reproduced as **Table 2**.

New cleaning chemistry: Convincing evidence must be presented that a new chemistry has a global warming potential (GWP) not greater than 100 (100 times greater than the global warming potential of CO₂), integrated over a 100-year interval.³

A. 1.2 Regional Environmental Impacts

A. 1.2.1 Volatile Organic Hazardous Air Pollutants (SCAQMD Clean Air Solvent Requirement)

No cleaning chemistry shall be certified when it contains more than 0.01% of chemicals on any of the following lists:

- "Hazardous Air Pollutants" (HAPs) list as contained in Section 112 (b)(1) of the 1990 Clean Air Act (used in the SCAQMD CAS protocol) (**Table 3**);
- "List of Toxic Substances" in Section 313 of the federal *Emergency Planning and Community Right-to-Know Act* (EPCRA) (**Table 4**); or
- "Substances for Which Emissions Must be Quantified" list in Appendix A-I of Proposed Amendments to the *Emission Inventory Criteria and Guidelines Report* published in accordance with the *Air Toxics* "Hot Spots" Information and Assessment Act of 1987 (AB 2588) (**Table 5**).

Lists two and three above are included in these criteria, but are not a part of the SCAQMD CAS protocol. All three of the lists noted above are included in the Tables section following these criteria.

United Nations Environment Programme (UNEP), February 1995, Scientific Assessment of Ozone Depletion: 1994, Chapter 13, "Ozone Depleting Potentials, Global Warming Potentials and Future Chlorine/Bromine Loading."

Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-1994

Page 10 Rev 24 2/9/98

¹ This list was formulated from the following sources:

 $^{^{2}}$ For instance, it would be acceptable to use CO_{2} that is either taken from the atmosphere, or captured from the waste stream of another industrial process.

³ For the sake of comparison, 1,1,1-TCA has a GWP (100-year integration) of 110.

A. 1.2.2 Reactivity (SCAQMD Clean Air Solvent Requirement)

No cleaning chemistry shall be certified when it contains more than 0.01% of chemicals on the "Maximum Incremental Reactivity" (MIR) list (**Table 6**). The chemicals on this list all have MIR values higher than toluene. This list is derived from SCAQMD's CAS protocol, and from Appendix VIII of the California Air Resources Board's *California Exhaust Emission Standards and Test Procedures for 1988 and Subsequent Model Passenger Cars, Light-Duty Trucks and Medium-Duty Vehicles*, as amended on September 22, 1993.

A. 1.2.3 VOC Content and Partial Pressure (SCAQMD Clean Air Solvent Requirement)

No cleaning chemistry shall be certified when, at its normal working strength (as specified in the manufacturer's instructions for its use), it contains a volatile organic compound (VOC) content greater than 50 grams/liter. VOC content will be determined by SCAQMD using its Method 313-91, Determination of Volatile Organic Compounds (VOC) by gas chromatography/mass spectrometry (GC/MS).

If the VOC content is less than 50 grams/liter, no cleaning chemistry which, at its normal working strength, has a VOC composite partial pressure (CPP) greater than 5 mm Hg at 20 °C shall be certified.

A. 1.3 Human Health Impacts

A. 1.3.1 Carcinogens

No cleaning chemistry shall be certified if, in its concentrated form, it contains more than 0.01% of a component on any of the following lists:

• International Agency for Research on Cancer (IARC) Group 1 or Group 2A or 2B⁴ chemicals (**Table 7**);

Page 11 Rev 24 2/9/98

⁴ IARC Group 1 refers to known human carcinogens. IARC Group 2 refers to suspected human carcinogens. Definitions of the IARC groups are as follows:

Group 1: The agent (mixture) is carcinogenic to humans. The exposure circumstance entails exposures that are carcinogenic to humans.

Group 2 (two classifications):

Group 2A: The agent (mixture) is probably carcinogenic to humans. The exposure circumstance entails exposures that are probably carcinogenic to humans.

- The National Toxicology Program (of the National Institute of Environmental Health Sciences) "Known Carcinogens" or "Reasonably Anticipated to be Carcinogens" (**Table 8**); or
- California Safe Drinking Water and Toxic Enforcement Act of 1986 (Proposition 65 Title 22, California Code of Regulations, Sections 12705 and 12709) chemical table entitled "No Significant Risk Levels for Carcinogens" (Table 9 (A)).

A. 1.3.2 Reproductive Toxicants

No cleaning chemistry shall be certified when it contains a component in a concentration greater than 0.01% of the concentrated form of the cleaning chemistry, and that component exceeds the *California Safe Drinking Water and Toxic Enforcement Act of 1986* (Proposition 65) "Acceptable Intake Levels for Reproductive Toxicants" (**Table 9 (B)**).

A. 1.3.3 Fire and Explosion Hazard

The flashpoint of the concentrated form of the cleaning chemistry must not be less than 140 degrees F. Furthermore, the flashpoint of the concentrated form of the cleaning chemistry must not be less than 40 degrees F above the manufacturer's recommended usage temperature. Flashpoints shall be measured using either the closed cup Penske-Marten method, or the Setaflash method.

A. 1.3.4 Corrosivity and Causticity

No cleaning chemistry having, at its most concentrated recommended working strength (as specified in the manufacturer's instructions), a pH either below 2.5 or above 11 shall be certified.⁵

Page 12 Rev 24 2/9/98

Group 2B: The agent (mixture) is possibly carcinogenic to humans. The exposure circumstance entails exposures that are possibly carcinogenic to humans.

Group 3: The agent (mixture, or exposure circumstance) is unclassifiable as to carcinogenicity in humans.

Group 4: The agent (mixture, exposure circumstance) is probably not carcinogenic to humans.

⁵ According to Grant's *Toxicology of the Eye*, the danger range for alkaline pH begins at 11 and increases markedly at 11.5. For acids, it begins at 2.5, much worse at 2 or below. For alkaline solutions, pH of 11 or below generally cause "only slight and reversible injury to the corneal stroma on brief (10 minute) exposure." <page 60> For acidic solutions: "Applied to human eyes, solutions from pH 7 down to pH 2 induce an increasingly strong stinging sensation, but on brief contact cause no damage." Page 46>. Grant, W. Morton, *Toxicology of the Eye*, Third Edition, Springfield, IL, 1986.

A. 1.3.5 General Health Hazard

No cleaning chemistry shall be certified when its concentrated form, contains more than 0.01% of any material with a National Fire Protection Association (NFPA) Health Hazard rating of either 3 or 4.

The *National Fire Protection Guide* (11th Edition, pages 704-11) defines these NFPA ratings as follows.

- A Health Hazard rating of 3 corresponds to "materials which on short exposure could cause serious temporary or residual injury."
- A Health Hazard rating of 4 corresponds to "materials which on very short exposure could cause death or major residual injury."

A. 1.4 Cautionary Substances

A. 1.4.1 Halogenated Cleaning Chemistries

No cleaning chemistry containing halogenated (chlorinated, brominated, iodized, or fluorinated) organic compounds of any kind will be certified, unless convincing evidence can be presented that the potential environmental impacts (including ozone depletion and global warming potentials) and health impacts (including acute and chronic health effects) are insignificant.

Stage A. 2 criteria will be applied to cleaning chemistries meeting Stage A. 1 criteria.

Stage A. 2.0 Performance Verification

Manufacturers pursuing certification of their cleaning chemistries must provide the names, addresses, phone numbers, and points of contact for at least ten shops currently using the cleaning chemistry⁶. These shops must be satisfied with its performance. Applicants should select facilities that represent:

- a wide spectrum of shop sizes,
- various numbers of employees, and
- different cleaning methods.

Page 13 Rev 24 2/9/98

⁶ The shops must be using the cleaning chemistry in a manner consistent with manufacturers' instructions and cautions.

It is advisable that both large and small businesses be included, as well as both manual and automated cleaning operations. Several types of cleaning application equipment should be represented—sprays and immersion baths, closed and open systems—depending on the nature of the certification(s) sought by the Applicant.

When contacted by the Expert Panel, the points of contact in the shops will be requested to provide information on their operations involving the cleaning chemistry. (The Expert Panel is defined as a group of specialists from various fields related to issues arising in industrial cleaning. The Panel will help evaluate applications and make decisions on appeals.) Panelists will ask about the materials being cleaned, how the cleaning chemistry is delivered, how cleanliness is measured, the level of cleanliness achieved, and other similar questions.

Note: All proprietary product information supplied by the applicant, and labeled as such, will be treated in strict confidence.

Besides verifying that the candidate cleaning chemistry can be used successfully, these data will identify the particular types of applications (precision electronics cleaning, precision metal parts cleaning, or general purpose cleaning) for which the system is suitable. Of the ten or more shop names provided, the Applicant should supply information on at least three shops using the system in each application for which certification is desired. (For instance, if certification of the system as a precision metal parts cleaning chemistry is desired, then at least three shops using the candidate cleaning chemistry in this way should be provided).

Stage A. 3 criteria will be applied to cleaning chemistries meeting Stage A. 2 criteria.

Stage A. 3.0 Vendor Responsibility

Vendor instructions for using a cleaning chemistry must include clear directions on the proper and safe use of that product. Instructions must include information on the appropriate application equipment and personal protective equipment required for safe use of the cleaning chemistry. A cleaning chemistry will be certified for use only with the appropriate equipment.

Vendor literature must include information on the possible hazards of using the cleaning chemistry. The literature must specifically include information on skin and eye irritation, skin sensitization, and precautions to observe when using the cleaning chemistry. The vendor must also specify instructions for proper recycling or disposal of waste generated during normal use of the cleaning chemistry.

Consideration will be given to the manufacturer's or distributor's recommended handling/disposal options for the spent cleaning chemistry. Preference will be granted to cleaning chemistries that can be readily recycled or regenerated (provided that recycling capacity or technology is available at a reasonable cost). Recommendations for final disposition of the cleaning chemistry must clearly state whether: it must be managed as a hazardous waste;

Page 14 Rev 24 2/9/98

it can be sent to the sewer; pre-treatment is recommended; it can be recycled; it can be landfilled. (These recommendations are expected to apply to the cleaning chemistry in its original formulation before use. Additional considerations may apply to the cleaning chemistry in its spent condition, once foreign materials have been added by the cleaning process.) Guidance must not be misleading. For instance, claims that a cleaning chemistry is "biodegradable" should state explicitly whether they apply to the cleaning chemistry alone, or the cleaning chemistry and any foreign materials added during use. The recommendations must also specify any regulatory agencies to be consulted prior to final disposition of the spent cleaning chemistry. For example, instructions might read, "Before releasing this product to the sewer, contact your local waste water sanitation agency."

Product quality: It is important that the vendor guard against changes in the chemical composition of the cleaning chemistry that may alter its properties. These changes may come from variations in feedstock, or inadvertent mixing of different products. A certification will be issued only for a specified chemical composition. If a product's chemical composition is varied in any way, either intentionally or unintentionally, then the certification will no longer apply.

While not required for certification, it is strongly encouraged that vendors:

- conduct short seminars for customers on the safe, environmentally friendly way to use their products; and
- develop a "closed loop" recycling option for the wastes generated during normal use of their products. Vendors are encouraged to accept responsibility for how the product is used, and how the wastes are handled as well. A "total service concept" could be offered by the vendor, in which spent cleaning chemistries are collected and reconstituted or processed for disposal by the vendor. (Note: The vendor must have the proper hazardous waste permits in order to offer such an off-site recycling option to the user shops.)

Stage A. 4 criteria will be applied to cleaning chemistries meeting Stage A. 3 criteria.

Page 15 Rev 24 2/9/98

Stage A. 4.0 Site Inspection

At least three California facilities employing the cleaning chemistry will be selected by the Expert Panel for inspection by at least one Expert Panelist. (The entire Expert Panel, however, will evaluate the data collected.)

For each Certification Class sought (precision metal cleaning, precision electronics cleaning, or general purpose cleaning), at least one facility employing that particular type of cleaning will be inspected. Selected facilities will represent a wide spectrum of shop sizes, numbers of employees, and cleaning methods. It is advisable that both large and small businesses be included in the inspections, and both manual and automated cleaning operations be examined. Ideally, the Expert Panel would examine several types of cleaning application equipment—sprays and immersion baths, closed and open systems, etc.

Expert Panelists will observe practical applications of the product to identify any environmental and health issues not captured in previous criteria. The visit will also serve to verify users' comments on performance of the cleaning chemistry. Such issues may require that additional cautions or instructions be included in the manufacturer's product literature.

The inspector should attempt to answer the following questions.

- Does the cleaning chemistry exhibit any environmental or health problems (e.g., unpleasant odors or rashes) that are not identified in vendor literature?
- Are the cleaning chemistry use instructions clear and easy to follow?
- Are disposal instructions clear?
- Does the cleaning chemistry perform as required?
- Does the cleaning chemistry adequately replace currently used materials?
- Do any quality problems result from the use of this cleaning chemistry?
- Do users accept the cleaning chemistry for its stated uses?
- Does use of the cleaning chemistry change the nature of products being manufactured?
 Are these changes important to the customers who buy the products?
- Are changes required in the equipment, work procedures, or other cleaners already in use when the shop first adopts the cleaning chemistry? Do these changes have an impact on productivity or profitability?

STAGE B: ASSAYS, DATA-BASE SEARCHES AND MODELING

Stage B criteria will be applied to candidate cleaning chemistries that have successfully passed Stage A criteria. Stage B criteria involve data generated in biological or environmental assays. Before Stage B begins, the Applicant will be apprised of the cost of the assays and tests deemed necessary by the Expert Panel, and may choose to proceed with or halt the certification protocol.

Quality of data

The Expert Panel will examine all assay data provided, to establish that proper laboratory procedures were followed. Data more than ten years old will be scrutinized particularly closely. Information on the testing laboratory and its procedures will be collected.

Stage B. 1.0 Acute Toxicity

A candidate cleaning chemistry must satisfy either Section B1.1 or B1.2, or both.

B1.1 Mammalian Toxicity Assay

The Applicant must present data indicating that the complete cleaning chemistry, at either its concentrated or typical working strength (as specified in the manufacturer's instructions for use), has passed an acute ingestive, dermal, or inhalatory mammalian toxicity assay. Passing "grades" for several common bioassays are given below. Bioassays should be performed according to conventional methods such as those endorsed by the United States Environmental Protection Agency, Office of Prevention, Pesticides and Toxic Substances (OPPTS), or the Organization for Economic Cooperation and Development (OECD). Equivalent results from other mammalian bioassays can be submitted, and will be examined by the Expert Panel as possible substitutes for the tests described below.

A cleaning chemistry passes the acute toxicity criterion if it meets any of the following conditions⁷:

a. When administered <u>orally</u> to rats it exhibits a median lethal dose (LD₅₀) equal to or exceeding 500 milligrams per kilogram of body weight.

Page 17 Rev 24 2/9/98

⁷ These conditions were formulated from data in:

Walker, J.D., "Estimation Methods Used by the TSCA Interagency Testing Committee to Prioritize Chemicals for Testing: Exposure and Biological Effects Scoring and Structure Activity Relationships." *Toxicology Modeling*, Vol. 1, No. 2, 1995, pp 123-141, and

U.S. EPA *Health Effects Test Guidelines OPPTS 870.1200 - Acute Dermal Toxicity* (Public Draft),. U.S EPA Office of Prevention, Pesticides, and Toxic Substances, EPA 712-C-96-192, June 1996.

b. When administered by continuous <u>dermal</u> contact for 24 hours with the bare skin of albino rabbits or other common test species such as rats or guinea pigs, it exhibits a median lethal dose (LD₅₀) equal to or exceeding 50 milligrams per kilogram of body weight.

c. When administered in air by continuous <u>inhalation</u> for one hour to rats, it exhibits a median lethal concentration (LC_{50}) equal to or exceeding 50 milligrams per liter.

B1.2 Alternative Evidence

When data on the complete cleaning chemistry is not available or practical to obtain, the Applicant must then present evidence that each of the chemical components in the cleaning chemistry passes one of the above conditions.

Stage B. 2.0 Chronic Toxicity

Cleaning chemistries containing at least 0.01% of any chemical that has entered the industrial cleaning market within the last ten years (e.g., hydrofluoroethers, chlorobromomethane, fluoroiodocarbons) must be examined in detail. It is possible that these chemistries may not have been evaluated by organizations such as IARC or the National Institute of Environmental Health Sciences. For cleaning chemistries that have not been evaluated, additional data are needed.

The Expert Panel may also find that certain older chemicals in a candidate cleaning chemistry have not been sufficiently evaluated as to their chronic toxicities. In this case, these chemicals, too, would be subject to this criterion.

For each chemical of concern in a cleaning chemistry, the following information must be obtained, either through toxicological assays, literature searches, or through a modeling technique similar to the one described below. The data collected must indicate that, under the conditions of use specified in manufacturers' operating instructions, the toxicity of the chemicals appears to be low.

Rodent carcinogenicity (male and female mice and rats) Developmental toxicity potential Mutagenicity (Ames and/or Dominant Lethal Test)

B 2.1 Metric for Interpreting Toxicological Results

The Interagency Testing Committee (ITC) methodology for "scoring" toxicological information will be used to evaluate chronic toxicity data.⁸ In **Table 10**, toxicity ranges are defined and given scores of 0 to 3. A score of 3 corresponds to an extremely toxic substance, and 0 is the "best" score, indicating only slight toxicity. For a cleaning chemistry to be certified, its toxicity (established from either assays, literature search test data, or toxicological modeling) must be in a range that corresponds to a score of 0.⁹ A cleaning chemistry scoring higher shall not be certified.

B 2.2 Toxicological Modeling Approach

TOPKAT is a software modeling system used by such U.S. agencies as the EPA and the Food and Drug Administration, as well as by various corporations (CIBA-GEIGY, 3M, Bristol-Meyers, Clairol, Sandoz, and many others). It computes expected toxicological and environmental effects, based on the molecular structure of a chemical. It utilizes quantitative structural activity relationship (QSAR) methodologies, and is currently used at LLNL and other national labs and universities. Using TOPKAT, a chemist requires about four hours to estimate the carcinogenicity, developmental toxicity and mutagenicity for each chemical. If a modeling technique is requested by the Applicant, either TOPKAT or a similar modeling method must be employed. The Expert Panel will determine if an alternative model is sufficiently reliable to generate meaningful data for the certification.

Stage B. 3.0 Environmental Impact

Environmental risks not adequately investigated in Stage A may also be investigated. The Expert Panel will determine the necessity of collecting additional environmental impact data on the product before issuing a certification. The Expert Panel may require additional testing of the product, additional information from the vendor, or a modification in the manufacturer's instructions for use. Panelists will consider likely use scenarios of the product, as well as potential release pathways of the wastes generated. They will examine such parameters as the product's biodegradability, its potential for bioaccumulation, and the impacts of any substances such as chelating agents and biocides. Breakdown products will also be considered. Concerns

⁸Walker, JD "Estimation Methods Used by the TSCA Interagency Testing Committee to Prioritize Chemicals for Testing: Exposure and Biological Effects Scoring and Structure Activity Relationships." *Toxicology Modeling*, Vol. 1, No. 2, 1995, pp 123-141.

⁹ For carcinogenicity and developmental toxicity, a score of 0 indicates negative results in two animal species. For mutagenicity, a score of zero corresponds to negative results in more than one system.

may be raised if the cleaning chemistry's structure is similar to known "problem" chemicals. New cleaning chemistries will receive particularly careful scrutiny.

Appeals Procedure

The appeals procedure gives Applicants a route to address aspects of the criteria for which they feel their product needs special consideration, or to challenge the criteria process when their product does not pass. An appeal should contain the following:

- identification of the criteria for which the Applicant feels an exception should be made;
 and
- presentation of substantial evidence supporting that exception.

The Expert Panel will hear appeals. Grounds for considering an exception to the criteria include the following situations.

- The criterion disqualifying the cleaning chemistry does not apply to the situation. For example, some metasilicates have high pH levels that would disqualify them, but certain metasilicates do not present a serious danger to the human eye. Since eye protection was the basis for the pH criteria, this argument might be used to make an exception.
- A unique application exists, for which no other cleaning technology performs adequately while offering lower environmental and human health risks. In this case, the technology would be certified only for the unique application.
- The cleaning chemistry is supplied along with application equipment that provides a reduced-risk, "controlled environment." Certain solvents can be used with equipment that reduces emissions and worker exposure, and the vendor's recycling policies limit releases to the environment. Any certification for such a system would be granted only for the solvent/equipment combination, not for the solvent by itself.

Page 20 Rev 24 2/9/98

Periodic Review Requirements

All certified cleaning chemistries must undergo re-examination every three years, for the purpose of re-approving the technology. Recertification analysis is conducted in considerably less detail than the original analysis. Recertification analysis would establish that the original estimates of human or environmental health risks and the efficient performance of the cleaning system remain substantially unchanged. Any evidence of degradation to human or environmental health, or reduced performance would require retesting and recertification.

If changes are made to the chemical composition of a cleaning chemistry, the manufacturer must notify DTSC immediately (or as soon as it becomes aware of the changes). Modifications to a cleaning chemistry may be intentional, to enhance its properties, or may result from a change of raw materials suppliers. Modifications can also result when a supplier buys its chemicals from a new source that may introduce different impurities into them. DTSC will analyze the changes to the cleaning chemistry and determine whether a recertification process is necessary.

Page 21 Rev 24 2/9/98

TABLES

Table 1	Known Ozone Depleting Compounds Source: South Coast Air Quality Management District
Table 2	Compounds with Global Warming Potentials Source: South Coast Air Quality Management District
Table 3	Hazardous Air Pollutants (HAPs) Source: Section 112 (b)(1) of the 1990 Clean Air Act
Table 4	Toxic Substances Source: Section 313 of the Federal Emergency Planning and Community Right-to-Know Act (EPCRA)
Table 5	Substances for Which Emissions Must be Quantified Source: Appendix A-I of Proposed Amendments to the Emission Inventory Criteria and Guidelines Report Published in Accordance with the Air Toxics "Hot Spots" Information and Assessment Act of 1987 (AB 2588)
Table 6	Maximum Incremental Reactivity (MIR) Source: Appendix VIII of the California Air Resources Board's California Exhaust Emission Standards and Test Procedures for 1988 and Subsequent Model Passenger Cars, Light-Duty Trucks and Medium-Duty Vehicles, as amended on September 22, 1993
Table 7	Group 1, 2A and 2B Chemicals Source: International Agency for Research on Cancer
Table 8	"Known Carcinogens" and "Reasonably Anticipated to be Carcinogens" Source: National Toxicology Program
Table 9	(A) "No Significant Risk Levels for Carcinogens" and (B) "Acceptable Intake Levels for Reproductive Toxicants" Source: California Safe Drinking Water and Toxic Enforcement Act of 1986 (Proposition 65)
Table 10	Biological Effects Scores Source: Interagency Testing Committee

Known Ozone Depleting Compounds

Source: South Coast Air Quality Management District Clean Air Solvent Certification Protocol, Appendix III, "Ozone Depleting Compounds"

Compounds with Global Warming Potentials

Source: South Coast Air Quality Management District Clean Air Solvent Certification Protocol, Appendix IV, "Compounds with Global Warming Potential"

Hazardous Air Pollutants (HAPs)

Source: Section 112 (b)(1) of the 1990 Clean Air Act as reprinted in South Coast Air Quality Management District Clean Air Solvent Certification Protocol, Appendix II, "Hazardous Air Pollutants"

Toxic Substances

Source: EPA Emergency Planning and Community Right-to-Know Act (EPCRA) Section 313 "List of Toxic Chemicals"

August 1966

Substances for Which Emissions Must be Quantified

Source: California Environmental Protection Agency
Air Resources Board Staff Report
"Initial Statement of Reasons for Proposed Rulemaking"
Appendix A-I of Proposed Amendments to the Emission Inventory Criteria and Guidelines
Report Published in Accordance with the Air Toxics "Hot Spots" Information and Assessment
Act of 1987 (AB 2588)

May 1966, Issue date June 7, 1996

Maximum Incremental Reactivity (MIR)

Source: California Air Resources Board California Exhaust Emission Standards and Test Procedures for 1988 and Subsequent Model Passenger Cars, Light-Duty Trucks and Medium-Duty Vehicles, as amended on September 22, Appendix VIII, reprinted as South Coast Air Quality Management District Clean Air Solvent Certification Protocol, Appendix V, "Maximum Incremental Reactivity"

Group 1, 2A and 2B Chemicals

Source: International Agency for Research on Cancer "Overall Evaluations of Carcinogenicity to Humans"

Website data as of May 1997

Known Carcinogens and

Reasonably Anticipated to be Carcinogens

Source: International Agency for Research on Cancer National Toxicology Program, 7th Annual Report on Carcinogens

Website data as of June 1997

- (A) No Significant Risk Levels for Carcinogensand
- (B) Acceptable Intake Levels for Reproductive Toxicants

Source: California Environmental Protection Agency STATUS REPORT

California Safe Drinking Water and Toxic Enforcement Act of 1986 (Proposition 65)

January 1994

Biological Effects Scores

Source: Interagency Testing Committee J. D. Walker in *Toxicology Modeling*, Vol. 1, No. 2.

1995